VI.7 Dense Membranes for Anode-Supported All-Perovskite IT-SOFC

Rambabu Bobba (Primary Contact), W. Zhao, S. Ghosh, Vinay S. Reddy, Kourtney L. Jacksom, Selissa Mitchell (Students)
Solid State Ionics Laboratory, Department of Physics
Southern University and A&M College
Baton Rouge, Louisiana 70813
Phone: (225) 771-2493; E-mail: rambabu@grant.phys.subr.edu

DOE Project Manager: Lane Wilson
Phone: (304) 285-1336; E-mail: Lane.Wilson@netl.doe.gov

Objectives

- Synthesize fine, homogeneous, phase-pure perovskites in the form of bulk (powders) and thin films to be used as components for developing zero-emission solid oxide fuel cells (SOFCs) capable of operating at reduced temperatures (800°C).
- Study the effect of composition on the microstructure (grain size, grain boundaries, surface texture), magnitude of oxygen permeation, O_2 exchange rates and long-term stability.
- Measure the AC impedance at higher temperatures and investigate the effect of electrical conductivity on the electronic structure using X-ray absorption near edge spectroscopy (XANES) and extended absorption fine structure spectroscopy (EXAFS).
- Assemble all-perovskite-based SOFC made from a dense ceramic electrolyte membrane ($La_{0.8}Sr_{0.2}Ga_{0.875}Mg_{0.125}O_{3-x}$) sandwiched between porous electrodes (based on Ni as anode and electronically conducting $LaNi_{0.6}Fe_{0.4}O_3$ and/or $La_{0.8}Sr_{0.23}CoO_3$ ceramic cathode).
- Evaluate the cost, performance, power generation capabilities, and emissions of the above SOFC while optimizing the reduced-dimensionality structures needed to demonstrate a zero-emission unit by the end of the three-year period.
- Create an interest among African American undergraduate and graduate students to develop theses related to the development of all-perovskite-based anode-supported intermediate-temperature SOFCs (IT-SOFCs).

Introduction

There are two major obstacles that have to be solved to operate SOFCs at intermediate temperatures, including the performance of electrolyte and electrodes. Lowering the operating temperature is possible with the use of alternative materials, appropriate cell design and manufacturing routes. In the search for dense electrolyte materials, the perovskite-based systems (ABO_3) have been considered as alternative options, particularly because ABO_3 can take on a number of different structures and can be doped with aliovalent cations on both the A and B sites. They can also accommodate very large concentrations of anion vacancies into their structures. $LaGaO_3$-based perovskite-type oxides—in particular, Sr- and Mg-doped $LaGaO_3$ (LSGM)—exhibit high oxide ion conductivity. The exceptional structural and chemical compatibility of LSGM with $La_{0.9}Sr_{0.1}Co_{0.9}M_{0.1}O_3$ (M= Fe, Ni, Mn) as perovskite-based cathode, and Ni-based perovskite cermet as anode, makes it a unique electrolyte for all-perovskite-based IT-SOFCs.

Approach

There is a critical need to optimize the processing conditions to obtain well-sintered LSGM electrolytes at low temperatures for developing miniaturized SOFC cells and stacks working at 600-800°C. The single-phase LSGM with high sintered density is not easy to obtain by conventional solid state technique. One of the requisites for application as SOFC electrolytes is high sinterability. The extent of sintering depends on the mode of synthesis. The

solid state route results in hard agglomerates and coarser grains, which inhibit sintering to obtain dense electrolyte materials. In view of increasing importance to produce dense LSGM ceramics on a large scale with better phase purity at lower temperatures in a cost-effective manner for use as electrolytes, an investigation was carried out to study the effect of conventional and microwave-assisted sintering of the recycled LSGM samples obtained from the regenerative sol gel (RSG) route, which is a combination of solid state reaction and Pechini-type method. The ability to recycle the same sample and use different processing conditions to tailor the properties of LSGM samples makes our regenerative sol-gel technique innovative and cost-effective.

RSG, microwave-assisted synthesis, and solid state conventional synthetic techniques have been employed to prepare 1) several compositions of $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-(x+y)/2}$ as an electrolyte, 2) porous $LaNi_{0.6}Fe_{0.4}O_3$ and deposited LSGM electrolyte on $LaNi_{0.6}Fe_{0.4}O_3$ as anode, 3) porous $LaSrCrMnO_3$ to be used as cathode, and 4) $LaCrO_3$ to be used as an interconnector. These components will be assembled in LSGM electrolyte-supported configuration, which is usually prepared by densifying the LSGM electrolyte first and then applying the anode and cathode layers afterwards.

Results and Discussion

For the first time, the Sr- and Mg-doped $LaGaO_3$ ($La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-0.5(x+y)}$, LSGM) was regenerated to aqueous solution. LSGM with comparable quality to other solution routes was synthesized by sol-gel route from the regenerated solution. The LSGM solid was dissolved in hot doubly distilled water with pH adjusted in the range of 0.5 to 1.0. To 50 ml of the solution, 10 g of citric acid and 5 ml of glycerol were added and dissolved to form the regenerated solution for LSGM. $La_{0.8}Sr_{0.2}Ga_{0.85}Mg_{0.15}O_{2.825}$ (LSGM-2015) and $LaGaO_3$ were prepared through both the regenerative sol-gel (RSG) and conventional solid-state route at 1400°C. Figure 1 displays the complex-plane impedance spectroscopy measured at 325°C of the LSGM-2017 samples sintered at different temperatures for eight hours.

The LSGM pellets prepared by the two methods were compared in their X-ray diffraction (XRD),

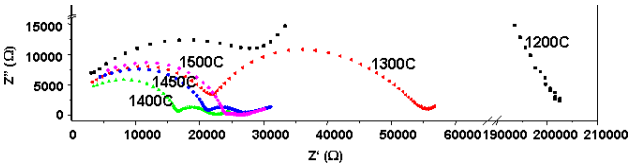

Figure 1. Complex Plane Plot of Impedance Spectroscopy Measured in Air at 325°C

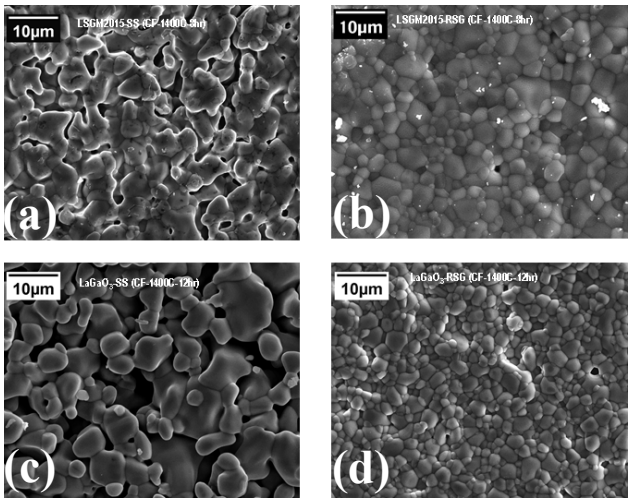

Figure 2. SEM Micrographs of $La_{0.8}Sr_{0.2}Ga_{0.85}Mg_{0.15}O_{2.825}$ (LSGM-2015) and $LaGaO_3$: (a) solid-state route precursor of LSGM-2015; (b) RSG route precursor of LSGM-2015; (c) solid-state route pellet of $LaGaO_3$; and (d) RSG pellet of $LaGaO_3$

scanning electron microscopy (SEM) (Figure 2), and electrochemical impedance spectroscopy (EIS) measurements. The LSGM-2015 synthesized via the RSG route exhibited conductivity $_t$ = 0.066 S/cm and 0.029 S/cm at 800°C and 700°C, respectively, and activation energy E_b= 0.97 eV, E_{gb}= 1.03 eV and E_t=1.01 eV for bulk, grain-boundary and whole material, respectively. Series of $La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17}O_{2.815}$ pellets were prepared by the RSG method at different sintering temperatures (1200-1500°C) and times. The sintering temperature severely affected the grain size (<0.1 m to 10 m) and the resistance (3 k to175 k) in all grain-boundary materials.

Ceria (CeO_2) and its substituted derivatives find immense potential as solid electrolytes in SOFCs, as oxygen sensor and as an automobile exhaust catalyst. Nano doped CeO_2 electrolyte shows promise with LSGM if they are used together either to block the

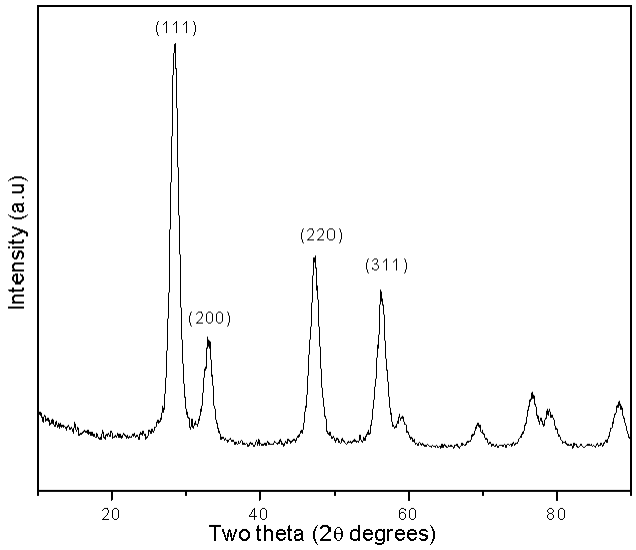

Figure 3. XRD of Nano CeO_2 Synthesized Using Hydrothermal Methods

electronic component in the doped ceria with the LSGM, or with the ceria, to block unwanted anode/electrolyte chemical reactions and/or to provide a catalytic surface for fuel oxidation at the anode. The surface layer on the anode side of these electrolytes can make these electrolytes viable for reduced temperature operations. In the past, fine CeO_2 powders have been prepared by using urea and hexamethylenetetramine-based precipitation. In these experiments, precipitation was carried out by conventional heating of the precursor solution at 80°C. We have prepared fine polycrystalline ceria powders at a temperature of 200°C by hydrothermal treatment of microwave-precipitated precursor from aqueous solution of $(NH_4)_2Ce(NO_3)_6$ and urea. Figure 3 shows the XRD pattern of nano CeO_2.

Simultaneously, we have also prepared nanocrystalline $Ce_{0.9}Gd_{0.1}O_{1.95}$ and lanthanide-doped ceria powders and multilayer thin films (using pulsed laser deposition) during this reporting period.

Future Plans

- We will attempt deposition of a thin layer of LSGM electrolyte on $LaNi_{0.6}Fe_{0.4}O_3$ cathode.
- We plan to carry out electrophoretic deposition of the dense LSGM samples on $LaNi_{1-x}Fe_xO_3$ porous cathodes presently being developed in our laboratory. To realize thin, dense O_2-semipermeable membranes on single crystalline substrates, we are preparing thin films using pulsed laser deposition (PLD). The technique of PLD seems very well suited to deposit prototype thin perovskite films with various compositions.
- Assembling and electrochemical measurements will be performed and will be reported in the future.

Summary

A promising perovskite cathode, electrolyte, and interconnect configuration was identified and synthesized. Three manuscripts were submitted for publication, and several presentations were made in national and international conferences.

One research associate and three (two graduate + one graduate) students were supported through this project at Southern University.